

## Regular Article

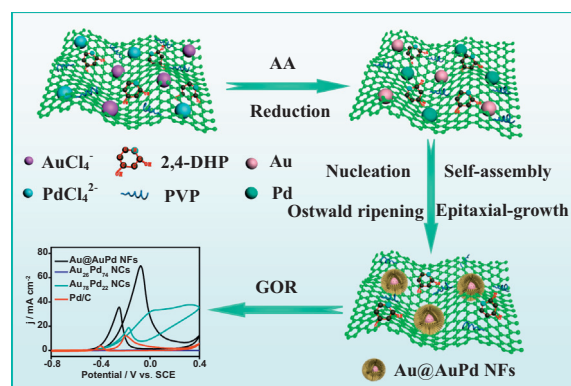
## One-pot fabrication of reduced graphene oxide supported dendritic core-shell gold@gold-palladium nanoflowers for glycerol oxidation



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Herein, a one-pot wet-chemical route was used to prepare well-defined dendritic core-shell gold@gold-palladium nanoflowers supported on reduced graphene oxide (Au@AuPd NFs/rGO), using 2, 4-dihydroxypyridine (2, 4-DHP) as a new stabilizer and structure-director. Their morphology, size, composition, and crystal structure were characterized by a set of characterization techniques. Control experiments demonstrated that the molar ratio of the metal precursors and the dosage of 2,4-DHP play essential roles in this synthesis. The growth mechanism of dendritic core-shell Au@AuPd nanoflowers was investigated in details. The synthesized branched architectures exhibited enlarged electrochemically active surface area (ECSA), improved catalytic properties, enhanced stability and durability toward glycerol oxidation in alkaline media when compared to the home-made Au<sub>26</sub>Pd<sub>74</sub> nanocrystals (NCs)/rGO and Au<sub>78</sub>Pd<sub>22</sub> NCs/rGO, along with commercially available Pd/C catalyst.

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## 1. Introduction

Among various types of direct alcohol fuel cells (DAFCs), alkaline fuel cells are widely explored because of the enhanced reaction kinetics and higher energy conversion efficiency [1]. Methanol,

ethanol and formic acid are widely used as the fuels in DAFCs, while their large-scaled applications are heavily hampered by the low energy density [2]. Recently, direct glycerol fuel cells have attracted increasing interest, thanks to the high theoretical power density, superior reactivity, low toxicity, and renewability of glycerol relative to methanol and ethanol counterparts [3]. For example, Zhang's group synthesized Ag@carbon nanocable-supported Pt nanoparticles for glycerol oxidation reaction (GOR) [4]. Wang

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and coworkers prepared bimetallic PdPt nanowire networks with improved glycerol catalytic activity [5]. However, the poor catalytic properties of anode and cathode catalysts are the major challenges for glycerol oxidation. Therefore, it is urgent to develop novel electrocatalyst with high conversion efficiency and durability for GOR [6].

To date, Pt and Pt-based nanomaterials are regarded as the most effective catalysts for alcohol oxidation [7,8]. Nevertheless, these catalysts often suffer from sluggish reaction kinetics and easily poisoning [9], as well as the high cost and scarce resources of Pt itself. As an alternative, Pd and Pd-based candidates receive significant attention for their relatively low cost and high storage [10], albeit with the much lower catalytic activity of Pd than Pt counterparts. This receives substantial interest for the research of highly efficient Pd-based catalysts [11].

To explore novel Pd-based catalysts with higher Pd utilization and superior catalytic activity, it is feasible to alloy Pd with another transition metal (e.g. Au, Cu, Ag, Co, and Ni). Now, a lot of Pd-based bimetallic nanocatalysts are synthesized, such as AuPd particles [12], PdAg hollow flowers [13], PtPd cubes [14] and PdCu sheets [15]. Among them, bimetallic AuPd nanocrystals have attracted extensive attention due to their superior catalytic performances in alcohol oxidation, vinylacetate synthesis and acetylene hydrogenation [16]. Specifically, the incorporated Au can oxidize the poisoning CO-like intermediates adsorbed onto the Pd active sites at the relatively lower potential, and eventually enhance the catalytic activity and strengthen the tolerance to the poisoning intermediates in the current system [17]. Besides, the synergetic effects between the bimetals in the AuPd systems greatly promote the sequential catalysis [18]. For example, Zhao and coworkers prepared Pd-on-Au nanoparticles (NPs) with enhanced catalytic activity and selectivity for glycerol oxidation [3]. Xu's group synthesized PdAu nanowire networks toward the oxidation of isopropanol and ethylene glycol [19]. Xia et al. fabricated Au@AuPd NPs with high-index facets for ethanol oxidation [20].

As well known, various support materials were utilized to retain the initial size, morphology and dispersity of the deposited catalysts, eventually improving the catalytic performances [21]. Graphene, a two-dimensional carbon sheet, has attracted substantial attention in catalysis because of its unique structure and properties [22] (e.g. large theoretical surface area, fast electron mobility and high electrical conductivity). Specially, reduced graphene oxide (rGO) is widely researched in electrochemical field recently owing to its enlarged electrochemical surface area and unique topological defects providing more catalytic active sites [23]. This means that rGO is particularly appropriate as a support to immobilize metallic catalysts [24].

Furthermore, the inter-structures of core-shell nanocatalyst significantly influence the catalytic performances [25]. Generally, dendritic frameworks contain more exposed active sites because of their sharp edges and rough surface [26]. Besides, the core-shell structures possess multifunctional capabilities and/or enhanced properties due to their conductive and versatile composition and structure, as well as the synergistic effects between the core and shell [27]. Impressively, the alloy core and/or shell has the cooperative interactions between the core and shell, along with the two metals, which is different from conventional core-shell structures like Au-core Pd-shell NPs [12]. Hence, the dendritic core-shell structure with tunable preparation was expected to improve the alcohol catalytic oxidation.

It is noted that the introduced capping agent would effectively regulate the morphology and size of the resultant nanocatalyst, eventually influencing the correlative catalytic behaviors [28]. As it is well known, 2, 4-dihydropyridine (2, 4-DHP, Fig. 1) contains rich hydroxyl and amine groups, which has strong chelating ability with the metal precursors and thereby affects the final morphology

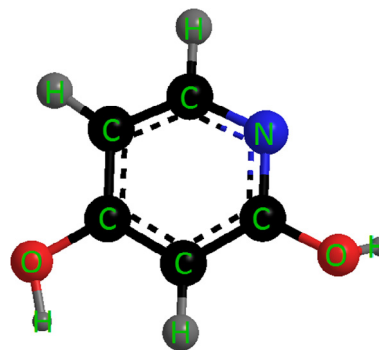


Fig. 1. The chemical structure of 2, 4-DHP.

of nanomaterials [29]. This is ascribed to the hydrogen-bonding and electrostatic interactions with the salt precursors [30].

Herein, a facile one-pot wet-chemistry route was utilized to prepare dendritic gold@gold-palladium nanoflowers supported on rGO (Au@AuPd NFs/rGO) in the existence of 2, 4-DHP and poly(vinylpyrrolidone) (PVP). The catalytic performance of the synthesized catalyst was investigated by using GOR as the benchmark system.

## 2. Experimental

### 2.1. Synthesis of Au@AuPd NFs/rGO

Typical synthesis of Au@AuPd NFs/rGO was described as follows. Firstly, 1.00 mL of the rGO suspension ( $0.5 \text{ mg mL}^{-1}$ ) pretreated by ultrasonication for 30 min, 200  $\mu\text{L}$  of  $\text{H}_2\text{PdCl}_4$  (100 mM) and 823  $\mu\text{L}$  of  $\text{HAuCl}_4$  (24.3 mM) were simultaneously injected into the 2, 4-DHP aqueous solution (75 mM) under magnetic stirring in a water bath at 25  $^\circ\text{C}$ . Then, 5.00 mL of the PVP solution (1%, w/v) was successively injected into the above mixed solution under stirring for 5 min, followed by putting 1.00 mL of the freshly-prepared ascorbic acid (AA) solution (100 mM) to the mixture. After continuously reacting for 30 min, the reaction system was remained static for 2 h. Finally, the resulting product was collected by centrifugation, thoroughly purified with ethanol and water, followed by drying in a vacuum for characterization.

In the controlled experiments, the other rGO supported AuPd products were synthesized by adjusting the molar ratios of the two precursors (Au:Pd) to 1:3 and 3:1, or the 2, 4-DHP concentrations, while the other experimental conditions were remained unchanged.

### 2.2. Construction of Au@AuPd NFs/rGO modified electrodes

For the electrochemical experiments, Au@AuPd NFs/rGO modified glassy carbon electrode (GCE) was firstly constructed. Typically, 2 mg of the product was dispersed into water (2.00 mL) and ultrasonicated for 30 min to obtain a homogeneous suspension. Afterward, 6  $\mu\text{L}$  of the suspension was dropped onto the electrode surface and dried at room temperature, followed by coating with another layer of Nafion (4  $\mu\text{L}$ , 0.05 wt%) and drying again in air. Besides, commercially available Pd/C (20 wt%) and the other rGO supported AuPd products modified electrodes were fabricated by the same way for comparison.

More detailed information of the materials, characterization and electrochemical experiments were presented in [Supporting Information \(SI\)](#).

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